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ON CHARLAND

WITNESS my hand this Eleventh day of April 2005

JANENE PEISKER

TEAM LEADER EXAMINATION

SUPPORT AND SALES

AUSTRALIA

Patents Act 1990

PROVISIONAL SPECIFICATION

Applicant:

Polymers Australia Limited

Invention Title: CERAMIFYING COMPOSITION FOR FIRE PROTECTION

The invention is described in the following statement:

CERAMIFYING COMPOSITION FOR FIRE PROTECTION

Field

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The present invention relates to fire barrier compositions which function by forming a ceramic at the elevated temperatures encountered in fire conditions. The invention also relates to the preparation of such compositions and their use, for example in shaping them to form articles that require fire barrier properties. The invention will be described with reference to cable applications however it will be understood that the composition may be used in providing fire barrier properties to a range of articles.

Background

For many applications it is desirable that a material used to provide fire protection exhibits limited and, preferably, no substantial change in shape following exposure to the elevated temperatures likely to be encountered in a fire situation (generally about 1000°C). If, under these conditions, the material shrinks significantly or its integrity is significantly disturbed by cracking and/or fracture this can lead to a breakdown in fire barrier properties and fire resistance. The fire barrier properties may be lost or be less effective than desirable for protecting susceptible components such as communications systems or power cables.

As will be apparent from the following, for many fire resistant polymeric compositions, the inherent shrinkage on exposure to elevated temperature is an accepted consequence of use. Specific measures taken to address this problem include the addition of intumescing agents, which cause expansion but provide a very mechanically weakened residue, or engineering design solutions which add to the cost of the final product or structure.

It is also desirable that a material used to impart fire resistance has acceptable mechanical strength for the intended application, following exposure to the elevated temperatures likely to be encountered in a fire situation, so that it can remain in place when subjected to the mechanical shocks and/or forces (eg from strong gas currents) associated with fire scenarios.

Electric cable applications typically consist of a central conductor surrounded by at least an insulating layer. Such cables find widespread use in buildings and indeed form the basis for almost all electric circuits in domestic, office and industrial buildings. In some applications, e.g. in emergency power supply circuits, there is a requirement for cables that continue to operate and provide circuit integrity even when subjected to fire, and there is a wide range of standards for cables of this type. To meet some of these standards, cables are typically required to at least maintain electrical circuit integrity when heated to a specified temperature (e.g. 650, 750, 950, 1050°C) in a prescribed manner and for a specified time (e.g. 15 min., 30 min., 60 min., 2 hours). In some cases the cables are subjected to regular mechanical shocks during the heating stage. They may be subjected to a water jet or spray either in the later stages of the heating cycle or after the heating stage.

To meet a given standard a cable is typically required to maintain circuit integrity throughout the test. Thus it is desirable that the insulation maintains low conductivity (even after prolonged heating at high temperatures), maintains its shape so it does not shrink and crack, and is mechanically strong, particularly if it is required to remain in place during shock such as that resulting from mechanical impact due to water jet or spray exposure. It is also desirable that the insulation layer remaining after heating will resist the ingress of water if the cable is required to continue operating during exposure to water spray for brief periods.

One method of improving the high temperature performance of an insulated cable has been to wrap the conductor of the cable with tape made with glass fibres and coated with mica. Such tapes are wrapped around the conductor during production and then at least one insulating layer is applied. Upon being exposed to increasing temperatures, the outer layer(s) are degraded and fall away, but the glass fibres hold the mica in place. These tapes have been found to be effective for maintaining circuit integrity in fires, but are quite expensive. Further, the process of wrapping the tape around the conductor is relatively slow compared with other cable production steps, and thus wrapping the tape slows overall production of the cable, again adding to the cost. A fire resistant coating that could be applied during the production of the cable (for example by extrusion) thereby avoiding the use of tapes, would be desirable.

A variety of materials have been used to impart fire resistance to structures and components, including electric cables. The use of compositions based on silicone elastomers has been reported. However, silicone elastomers can be expensive, have relatively poor mechanical properties and can be difficult to process, for example by extrusion techniques. Furthermore, these compositions tend to have

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the associated disadvantage that they are converted to powdery substances when exposed to fire as a result of the organic components of the silicone elastomers being pyrolised or combusted. The pyrolysis or combustion products are volatilised and leave an inorganic residue or ash (silicon dioxide) that has little inherent strength. This residue is generally not coherent or self-supporting and indeed is often easily broken, dislodged or collapsed. This behaviour mitigates against using silicone elastomers in passive fire protection. This means, for instance, that silicone polymers used as insulation on electric cables must be protected and held in place with physical supports such as inorganic tapes and braids or metal jackets.

Some materials, based on silicone polymers or other polymers in combination with various inorganic additives, retain their integrity and form self supporting ceramic on exposure to fire, and some of these have been proposed for use as insulation layers on electric cables that do not contain physical supports. Two examples are described below.

International Application No. PCT/AU03/00968 describes a fire resistant composition, which comprises a silicone polymer along with mica, and a glass additive in respective amounts from 5% to 30% and 0.3 to 8% by weight based on the total weight of the composition.

International Application No. PCT/AU03/01383 (the contents of which are herein incorporated by reference) describes a composition which contains an organic polymer, a silicate mineral filler and a fluxing agent (or precursor resulting in a fluxing agent) in an amount of from 1 to 15% by weight of the residue resulting from fire conditions.

25 **Summary**

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We have now found that integrity of a ceramic forming composition may be retained by using a composition comprising a component for forming an inorganic liquid phase at elevated temperature, a component providing a refractory filler and a dispersed gas phase formed in the liquid phase at elevated temperature.

We provide in accordance with a first aspect of the invention a ceramifying composition for forming a fire resistant ceramic at elevated temperatures the composition comprising:

(i) an inorganic refractory filler component preferably comprising a mineral silicate;

- (ii) an inorganic phosphate adapted to provide an inorganic liquid phase at temperatures encountered under fire conditions; and
- (iii) an organic polymer.

The inorganic liquid forming component provides a liquid phase matrix under fire conditions and entraps pores of a gas phase formed as a result of decomposition of the ceramifying composition at elevated temperatures under fire conditions.

The composition may and preferably will comprise an amount of from 10 to 20% by weight of at least one of hydroxides and oxides selected from least one of aluminium and magnesium. More preferably the composition comprises 10 to 20 % by weight of aluminium hydroxide.

The composition of the invention will typically form a self supporting ceramic at temperatures encountered under fire conditions. The porosity of the resulting ceramic is preferably in the range of from 20 vol% to 80 vol%. Preferably at least 40% of its total composition will be inorganic fillers.

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In a further aspect the invention provides a cable comprising an elongated conducting element and coating layers comprising the hereinbefore described ceramifying composition. Preferably the cable coatings comprise a plurality of layers including a layer comprising the hereinbefore described ceramifying layer and at least one (preferably inner) layer that either forms a mechanically weaker self supporting ceramic and/or at least one inner layer that thermally decomposes to deposit an inorganic residue that has low electrical conductivity.

In a particularly preferred embodiment of the composition of the invention there is provided a ceramifying composition for forming a fire resistant ceramic under fire conditions the composition comprising:

- (i) an inorganic refractory filler component preferably comprising a mineral silicate;
- (ii) an inorganic phosphate adapted to provide an inorganic liquid phase at temperatures encountered under fire conditions; and
- 30 (iii) an organic polymer.

The preferred inorganic refractory filler is mineral silicate filler.

The composition may and preferably will comprise an amount of from 10 to 20% by weight of at least one of hydroxides and oxides selected from least one of

aluminium and magnesium. More preferably the composition comprises 10 to 20 % by weight of aluminium hydroxide.

The composition of the invention will typically form a self supporting ceramic at temperatures encountered under fire conditions. The porosity of the resulting ceramic is preferably in the range of from 20 vol% to 80 vol%. Preferably at least 40% of its total composition will be inorganic fillers.

The composition forms a ceramic under fire conditions, the ceramic comprising a liquid matrix, dispersed refractory filler particles and dispersed pores of gas phase.

In a preferred embodiment of the invention the ceramic forming composition comprises:

at least 15% by weight based on the total weight of the composition of a polymer base composition comprising at least 50% by weight of an organic polymer; and

20-40% by weight of an inorganic phosphate, preferably ammonium polyphosphate, based on the total weight of the composition, and

an inorganic refractory filler comprising in an amount of at least 15% by weight based on the total weight of the composition preferably silicate mineral filler.

The composition may and preferably will comprise an amount of from 10 to 20% by weight of at least one of hydroxides and oxides selected from least one of aluminium and magnesium. More preferably the composition comprises 10 to 20 % by weight of aluminium hydroxide.

The composition of the invention will typically form a self supporting ceramic at temperatures encountered under fire conditions. The porosity of the resulting ceramic is preferably in the range of from 20 vol% to 80 vol%. Preferably at least 40% of its total composition will be inorganic fillers.

The composition generally forms a self-supporting and porous ceramic when exposed to fire rating temperatures and at least 40% of its total composition will be inorganic compounds.

Detailed Description

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The ceramifying composition of the invention provides fire barrier properties at temperatures encountered under fire conditions by forming a ceramic having a dispersed gas phase.

The ceramifying composition includes inorganic refractory fillers and inorganic phosphate which together form a coherent ceramic at temperatures encountered under fire conditions. Preferably at the elevated temperatures encountered under fire conditions the phosphate component will form a liquid matrix and decomposition of the ceramifying composition will form a dispersed gas phase of fine pores. The shrinkage associated with the formation of a liquid phase is compensated by the formation of uniformly dispersed fine pores in the liquid phase matrix enabling the composition to retain the original size and shape on conversion to ceramic. Uniform dispersion of the fine pores and the refractory inorganic filler particles increase the viscosity of the liquid matrix to a sufficiently high level for the composition to be self supporting at all stages of conversion into a ceramic under a fire situation.

On formation of the liquid phase at temperatures encountered under fire conditions the refractory inorganic filler particles are dispersed in and held together by the liquid phase matrix.

The composition of the invention comprises at least one phosphate liquid forming compound. The most preferred phosphate component will comprise ammonium polyphosphate.

Significant advantages are provided by using liquid forming compositions comprising phosphate glass forming systems. Phosphate glass forming systems and in particular systems based on ammonium polyphosphate have the significant advantage of maintaining their integrity in combination with the other components of the composition of the invention even when high proportions of these glass forming components are present relative to the other components. In a particularly preferred embodiment of the invention the inorganic phosphate liquid forming component is chosen to provide, in combination with other components, properties (particularly relatively high viscosity) which will entrap gas pores. If the viscosity of the liquid composition formed under these conditions is relatively low, the gas produced may be lost, resulting in an increased likelihood of failure through shrinkage and possibly also loss of the liquid component.

It is believed that the inorganic phosphate decomposes at a temperature at or below the decomposition temperature of the other components to phosphoric acid. In

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the case of ammonium polyphosphate, ammonia is also a decomposition product. The phosphoric acid dehydrates any organic material in its proximity initially forming a carbonaceous char which subsequently turns into a ceramic, while the ammonia may contribute to formation of a desirable level of porosity.

Viscosity of the liquid forming systems can and preferably is controlled by using a significant proportion of a compound (particularly ammonium polyphosphate) which forms a liquid which has a relatively high intrinsic viscosity at temperatures encountered under fire conditions.

Another approach which may be used to provide a sufficient viscosity to entrap gas involves factors extrinsic to the liquid forming component such as the relative quantity and type of filler that is used and the quantity and type of other components.

The viscosity which is optimal to entrap gas will of course depend on the types and volumes of gases generated and the proportions of organic components and any optional components such as processing aids and the like.

The more preferred liquid forming components are phosphate liquid forming components, most preferably ammonium polyphosphate. Phosphate liquid forming components are preferably present in an amount of from 15 to 40% by weight of the total composition and still more preferably from 20 to 40% by weight of thetotal composition.

Specific examples of inorganic phosphate components include compositions consisting at least of ammonium phosphate, ammonium polyphosphate, and melamine phosphate, As previously mentioned, ammonium polyphosphate offers significant advantages in the compositions of the invention.

Generally the liquid forming component will form a liquid at temperatures over 450°C.

The gas is produced by thermal decomposition of components in the composition including the organic components. Examples of inorganic gas producing materials include hydrated materials such as magnesium hydroxide and aluminiumhydroxide, carbonates such as magnesium carbonate and calcium carbonate. Examples of organic gas producing materials include organic polymers and any organic processing additives. Aluminium hydroxide is particularly preferred as it also contributes to the refractory filler component by virtue of the formation of alumina.

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It is particularly preferred that the gas generating component is finely divided and distributed throughout the ceramic forming component.

The gas-generating component may comprise a mixture of compounds that generate gas at elevated temperatures. Preferably the gas-generating component will generate at least a portion of gas above the temperature at which the inorganic liquid forming component forms a liquid.

The composition of the invention will typically form a self supporting ceramic at temperatures encountered under fire conditions. The porosity of the resulting ceramic is preferably in the range of from 20 vol% to 80 vol%. Preferably at least 40% of its total composition will be inorganic fillers.

The compositions in accordance with the present invention also include an inorganic refractory filler preferably a silicate mineral filler. Such fillers typically include alumino-silicates (e.g. kaolinite, montmorillonite, pyrophillite — commonly known as clays), alkali alumino-silicates (e.g. mica, felspar, spodumene, petalite), magnesium silicates (e.g. talc) and calcium silicates (e.g. wollastonite). Mixtures of two or more different silicate mineral fillers may be used. Such fillers are commercially available. Silicon dioxide (silica) is not a silicate mineral filler in the context of the present invention.

The composition typically comprises at least 15% by weight, preferably at least 25% by weight silicate mineral filler. The maximum amount of this component tends to be dictated by the processability of the composition.

In addition to mineral silicate fillers, a wide range of other inorganic fillers may be added. Preferred additional inorganic fillers are hydroxides or oxides of magnesium and aluminium. Also inorganic fibres which do not melt at 1000°C can be incorporated including aluminium oxide fillers.

The composition may and preferably will comprise an amount of from 10 to 20% by weight of at least one of hydroxides and oxides selected from least one of aluminium and magnesium. More preferably the composition comprises 10 to 20 % by weight of aluminium hydroxide.

The composition of the invention will typically form a self supporting ceramic at temperatures encountered under fire conditions. The porosity of the resulting ceramic is preferably in the range of from 20 vol% to 80 vol%. Preferably at least 40% of its total composition will be inorganic fillers.

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Additional fillers may be refractory or non-refractory in nature. Refractory fillers additional of any mineral silicate will form part of the refractory inorganic filler component. Non-refractory fillers may form part of the liquid matrix, together with the inorganic phosphate, at temperatures encountered under fire conditions.

The composition of the invention comprises an organic polymer. An organic polymer is one that has an organic polymer as the main chain of the polymer. Silicone polymers are not considered to be organic polymers, however, they may be usefully blended with the organic polymer(s), as the minor component, and beneficially provide a source of silicon dioxide (which assists in formation of the ceramic) with a fine particle size when they are thermally decomposed. The organic polymer can be of any type, for example a thermoplastic polymer, a thermoplastic elastomer, a cross-linked elastomer or rubber, a thermoset polymer. The organic polymer may be present in the form of a precursor composition including reagents, prepolymers and/or oligomers which can be reacted together to form at least one organic polymer of the types mentioned above. Additional fillers may be present which may be refractory or non-refractory in nature. Additional refractory fillers will contribute to the refractory organic filler component. Non-refractory fillers may form part of the liquid phosphate matrix at temperatures encountered under fire conditions. Preferably, the organic polymer can accommodate high levels of the inorganic components required to form the ceramic, whilst retaining good processing and mechanical properties. It is desirable in accordance with the present invention to include in the fire resistant compositions high levels of the inorganic components as such compositions tend to suffer reduced weight loss on exposure to fire when compared with compositions having lower levels of the inorganic components. Compositions loaded with relatively high concentrations of inorganic components are therefore less likely to shrink and crack when ceramified by the action of heat.

It is also advantageous for the chosen organic polymer not to flow or melt prior to its decomposition when exposed to the elevated temperatures encountered in a fire situation. The most preferred polymers include ones that are cross-linked after the fire resistant composition has been formed, or ones that are thermoplastic but have high melting points and/or decompose to form a char near their melting points; however, polymers that do not have these properties may also be used. Suitable organic polymers are commercially available or may be made by the application or

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adaptation of known techniques. Examples of suitable organic polymers that may be used are given below but it will be appreciated that the selection of a particular organic polymer will also be impacted by such things as the additional components to be included in the fire resistant composition, the way in which the composition is to be prepared and applied, and the intended use of the composition.

Organic polymers suitable for use with this invention include thermoplastic polymers, thermoset polymers, and (thermoplastic) elastomers. Such polymers may comprise at least one polymer selected from the group consisting of homopolymers and copolymers of polyolefins, vinyl polymers, acrylic and methacrylic polymers, styrene polymers, polyamides, polyimides, epoxides, polyoxymethylene acetals, polycarbonates, polyurethanes, polyesters, phenolic resins and melamine-formaldehyde resins.

The organic polymers that are particularly well suited for use in making coatings for cables are:

commercially available thermoplastic and crosslinked polyethylenes with densities from 890 to 960 kg/litre, copolymers of ethylenes of this class with acrylic and vinyl other olefin monomers, terpolymers of ethylene, propylene and diene monomers, so-called thermoplastic vulcanisates where one component is crosslinked while the continuous phase is thermoplastic and variants of this where all of the polymers are either thermoplastic or crosslinked by either peroxide, radiation or so-called silane processes

Compositions of the invention may be formed about a conducting element or plurality of elements by extrusion (including co-extrusion with other components) or by application of one or more coatings.

As noted, the organic polymer chosen will in part depend upon the intended use of the composition. For instance, in certain applications a degree of flexibility is required of the composition (such as in electrical cable coatings) and the organic polymer will need to be chosen accordingly based on its properties when loaded with additives. Polyethylenes and ethylene propylene elastomers, have been found to be particularly useful for compositions for cable coatings. Also in selecting the organic polymer account should be taken of any noxious or toxic gases which may be produced on decomposition of the polymer. The generation of such gases may be more tolerable in certain applications than others. Preferably, the organic polymer used is halogen-free.

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As noted the polymer base composition may include a silicone polymer. However, in this case the organic polymer would usually be present in the polymer base composition in a significant excess when compared with the silicone polymer. Thus, in the polymer base composition the weight ratio of organic polymer to silicone polymer may be from 5:1 to 2:1, for instance from 4:1 to 3:1. In terms of weight percentage, if present, the silicone polymer might generally be present in an amount of from 2 to 15% by weight based on the total weight of the formulated fire resistant composition. When a combination of organic and silicone polymers are used, high concentrations of silicone polymer can present processing problems and this should be taken into account when formulating compositions in accordance with the present invention.

The composition of the invention typically comprises at least 15% by weight based on the total weight of the composition of a polymer base composition comprising at least 50% by weight of an organic polymer.

The upper limit for the amount of polymeric components in the fire resistant composition tends to be influenced by the desired properties of the formulated composition. If the amount of the polymeric components exceeds about 60% by weight of the overall composition, it is unlikely that a cohesive, strong residue will be formed during a fire situation. Thus, the base composition generally forms from 15 to 60%, preferably from 20 to 50%, by weight of the formulated fire resistant composition.

The organic polymer is present in the polymer base composition in an amount of at least 50% by weight. This facilitates loading of the polymeric base composition with the additional components without detriment to the processability of the overall composition. As noted the based composition may include a silicone polymer. However, in this case the organic polymer would usually be present in the base composition in a significant excess when compared with the silicone polymer.

Usually after exposure of the composition at elevated temperature (to 1000°C) the residue remaining will generally constitute at least 40%, preferably at least 55% and more preferably at least 70% by weight of the composition before pyrolying. Higher amounts of residue are preferred as this may improve the ceramic strength at all temperatures.

The compositions of the present invention may be provided in a variety of different forms, including:

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- As a sheet, profile or complex shape. The composition may be fabricated into these products using standard polymer processing operations, eg extrusion, moulding (including hot pressing and injection moulding). The products formed can be used in passive fire protection systems. The composition can be used in its own right, or as a laminate or composite with another material (for example, plywood, vermiculite board or other). In one application the composition may be extruded into shapes to make seals for fire doors. In the event of a fire, the composition is converted into a ceramic thus forming an effective mechanical seal against the spread of fire and smoke.
- As a pre-expanded sheet or profile. This form has additional benefits compared with the above, including reduced weight and the capacity for greater noise attenuation and insulation during normal operating conditions. Porosity can be incorporated into the material during manufacture of the sheet or profile by thermal degradation of a chemical blowing agent to produce a gas product, or by physically injecting gas into the composition during processing before curing.
 - 3. As an intumescent product, which expands by foaming when exposed to heat or fire. In this application the product can be used, for example, around pipework or penetrations between walls. In the event of a fire the product expands to fill the void and provide an effective plug to prevent the spread of fire. The intumescent material may be in the form of an extrudable paste or a flexible seal.
 - 4. As a mastic material which can be applied (for example from a tube as per a conventional silicone sealant) as a seal for windows and other articles.
- 25 5. As paint, or an aerosol-based material, that could be sprayed or applied by with a brush.

Specific examples of passive fire protection applications where this invention may be applied include but are not limited to firewall linings for ferries, trains and other vehicles, fire partitions, screens, ceilings and linings coatings for building ducts; gap fillers (i.e. mastic applications for penetration), structural fire protection [to insulate the structural metal frame of a building to allow it to maintain its required load bearing strength (or limit the core temperature) for a fixed period of time], fire door inserts, window and door seals, intumescent seals, and compounds for use in

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electrical boxes, in fittings, straps, trays etc that are attached to or used to house cables or similar applications.

Another area of application is in general engineering. Specific areas of general engineering, where passive fire protection properties are required, include transportation (automotive, aerospace, shipping), defence and machinery. Components in these applications may be totally or partially subject to fire.

When totally subject to fire, the material will transform to a ceramic, thereby protecting enclosed or separated areas. When partially subjected to fire, it may be desirable for a portion of the material to transform to ceramic, being held in place by the surrounding material that has not transformed to a ceramic. Applications in the transport area may include panelling (eg in glass fibre reinforced thermoplastic or thermoset composites), exhaust, engine, braking, steering, safety devices, air conditioning, fuel storage, housings and many others. Applications in defence would include both mobile and non-mobile weapons, vehicles, equipment, structures and other areas. Applications in the machinery area may include bearings, housing barriers and many others.

The compositions of the present invention are especially useful as coatings for the production of cables for example they can be used for insulation or sheathing layers. The compositions are therefore suitable for the manufacture of electrical cables that can provide circuit integrity in the case of fire.

Description of the Drawings

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Figure 1 is a perspective view of a cable having a ceramic forming insulation layer in accordance with the invention;

Figure 2 is a perspective view of a multiconductor cable in which compositions of the invention are used as a sheath.

Figures 1 and 2 show single and multiconductor cables 1, 10 respectively which have an insulation layer 2, or layers 12 and having additional ceramifying layers 4, 14 of a composition in accordance with the invention. In both of these cable designs, the position of the insulation layer and the ceramifying layer in accordance with the invention can be interchanged depending on the role of the additional layer.

In the design of such cables the ceramic forming insulation layers can be extruded directly over conductors and the ceramifying layers extruded over an insulation layer or layers. Alternatively, they can be used as an interstice filler in

multi-core cables, as individual extruded fillers added to an assembly to round off the assembly, as an inner layer prior to the application of wire or tape armour.

Figure 3 shows a possible design for a fire performance article 1 and Figure 4 shows a cross section at the position II in Figure 3. The metal substrate 2 has a protective coating 6 which comprises at least one ceramic forming layer 11 and at least one ceramifying layer in accordance with the invention.

In the first embodiment of the cable of the invention as shown for example in Figure 1 a functional element such as copper conductor is surrounded by a ceramifying insulation composition which forms a relatively weak ceramic which in turn is surrounded by a ceramifying composition in accordance with the invention for forming a fire resistant ceramic under fire conditions the composition comprising:

- (i) an inorganic refractory filler component preferably comprising a mineral silicate;
- (ii) an inorganic phosphate adapted to provide an inorganic liquid phase at temperatures encountered under fire conditions; and
- (iii) an organic polymer.

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The inorganic liquid forming component provides a liquid phase matrix under fire conditions and entraps pores of a gas phase formed as a result of decomposition of the ceramifying composition at elevated temperatures encountered under fire conditions.

Compositions in accordance with the current invention are well suited for use imparting fire resistance to structures and components. Some of the compositions may be suitable for use as the sole insulation layer on electric cables, particularly where they exhibit suitable high electrical resistivity at elevated temperature. For those compositions that do not meet this requirement, it may be desirable to incorporate an additional layer that is electrically insulative at high temperature to ensure circuit integrity.

For instance, a composition which imparts thermal resistance and/or provides a physical barrier at elevated temperature but which becomes electrically conducting may be provided about a layer adapted to provide electrical insulation.

In a particularly preferred embodiment of a cable in accordance with the invention there is another layer of a ceramifying material, axially inward from a strong ceramifying materials described in accordance with the composition of the invention. The axially inward layer may be of a range of types and may be a second layer in

accordance with the composition of the present invention. It is particularly preferred, however, that in the cable in accordance with this embodiment that the layer axially inwards of a layer in accordance with a composition of the present invention is of the type described in our co pending International Patent Application No PCT/AU03/01383 the contents of which are herein incorporated by reference.

The use of an insulation layer of this type, that forms a self supporting ceramic on exposure to fire, in combination with a layer (preferably an outer layer) made from compositions in accordance with the current invention typically has the advantage of providing a mechanically stronger coating over the conductor after exposure to fire.

The resulting cable is more likely to remain in place when subjected to the mechanical shocks and/or forces (eg from strong gas currents) associated with fire scenarios.

However, the composition of the invention may also be used in combination with ceramifying compositions which provide inferior mechanical strength at temperatures encountered under fire conditions. Thus on exposure to elevated temperatures, compositions in accordance with the present invention may form a physically strong coherent layer over an insulating layer, that is degraded to inorganic residues that are not coherent, around an electrical conductor and therefore do away with the need to use physical supports.

The ceramifying insulating layer and layer in accordance with the composition of the invention may be applied by conventional means such as extrusion.

In a further embodiment of the cable of the invention a copper conductor is surrounded by a filled organic polymer layer which decomposes to deposit a loosely packed electrically insulative inorganic powder (e.g. silicon dioxide, aluminium oxide, magnesium oxide) in the resulting gap between the conductor and the ceramifying layer of the composition of the present invention on exposure to temperatures encountered under fire conditions.

The outer layer of the cable is a composition in accordance with the invention comprising:

- 30 (i) an inorganic refractory filler component preferably comprising a mineral silicate;
 - (ii) an inorganic phosphate adapted to provide an inorganic liquid phase at temperatures encountered under fire conditions; and
 - (iii) an organic polymer.

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The inorganic liquid forming component provides a liquid phase matrix under fire conditions and entraps pores of a gas phase formed as a result of decompositions of the ceramifying composition at elevated temperatures encountered under fire conditions.

This extrusion may be carried out in a conventional manner using conventional equipment. The thicknesses of the layers of insulation will depend upon the requirements of the particular standard for the size of conductor and operating voltage. Typically the insulation will have a total thickness from 0.6 to 3 mm. For example, for a 35 mm² conductor rated at 0.6/1 kV to Australian Standards would require an insulation thickness of approximately 1.2 mm. The cable may include other layers such as a cut-resistant layer and/or sheathing layer.

Furthermore, at elevated temperatures the compositions may also yield residue which is coherent and has good mechanical strength, even after cooling. The residue is self-supporting and will be retained in its intended position rather than fracturing and being displaced, for example, by mechanical shock. In this context the term "residue" is hereinafter intended to describe the product formed when the composition is exposed to an elevated temperature, experienced under fire conditions. Generally an elevated temperature of 1000°C for 30 minutes is sufficient to covert fire resistant compositions of the invention to residue. Desirably, as well as providing thermal insulation and/or a coherent physical barrier or coating, compositions in accordance with the present invention may also exhibit the required electrical insulating properties at elevated temperatures.

The present invention describes materials that typically meet the requirements of providing no substantial change in shape when exposed to the elevated temperatures likely to be encountered in a fire situation (generally about 1000°C) producing ceramics that are self supporting and have acceptable mechanical strength.

It has been found that compositions in accordance with the present invention may form a coherent ceramic product when exposed to elevated temperatures and that this product exhibits desirable physical and mechanical properties. The ceramic char formed after exposure of compositions of the present invention at an elevated temperature not in excess of 1050°C preferably has a flexural strength of at least 2MPa. It is a distinct advantage that the compositions are self-supporting, i.e. they remain rigid and do not undergo heat induced deformation or flow. They also

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undergo little if any shrinkage following high temperature exposure, whether the heating rate experienced is relatively fast or slow. Typically rectangular test specimens will undergo changes in linear dimension along the length of the specimen of less than 10%, Generally speaking the limit on contraction is more important preferably this is less than 5% and more preferably less than 1% and most preferably essentially none. In the case of expansions, any expansion is less than 10% and preferably 5% and most preferably less than 3%. Changes in dimensions are also influenced by additional factors including the thermal degradation behaviour of the components, particularly if organic polymeric components are present and can vary from shrinkage to expansion, (caused by gases escaping from decomposing components of the composition) with expansion having the most pronounced effect (in a percentage change basis) in the least constrained dimension such as the thickness (height) of the specimen. Thus one skilled in the art can select the components of the composition to achieve a range of outcomes under the expected heating conditions, for example: no significant change in linear dimensions, no substantial change in all three dimensions (net shape retention), an increase in linear dimensions of under 5%, etc.

It is a further advantage, of the compositions of the present invention, that this type of coherent product with desirable physical and mechanical properties can be formed at temperatures well below 1000°C. The compositions of the invention may be used in a variety of applications where it is desired to impart fire resistance to a structure or component. The compositions are therefore useful in passive fire protection systems.

For fire protection applications, it is preferable that this change in linear dimension is less than 10% and more preferably less than 5%, and most preferably less than 1%. As explained, preferably the compositions exhibit minimal linear dimensional change after exposure to the kind of temperatures likely to be encountered in a fire. By this is meant that the maximum linear dimensional change in a product formed from a composition in accordance with the present invention is less than 10%, preferably less than 5% and most preferably less than 1%. In some cases net shape reduction is the most preferred.

In this paragraph we describe a test we have found useful in examining dimensional stability. Specimens of nominal dimensions 30 mm x 13 mm x 1.7 mm, made from the composition are placed on a rectangular piece of refractory so that

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their long axis was perpendicular to one edge of the supporting refractory block and a 13 mm long portion of each specimen is projecting from the edge of the supporting refractory block. They are then heated at 12°C per minute to 1000°C and maintained at this temperature for 30 minutes in air. At both temperatures, the specimens of composition remain coherent and self-supporting and retain the shape of the specimen prior to exposure to elevated temperatures. The change in dimensions of the particularly preferred compositions along the length and the width is less than 5%.

The invention will now be described with reference to the following non-limiting examples.

Examples

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Example 1

A two-roll mill was used to prepare the compositions denoted A, B, C and D in Table 1. In each case, the EP polymer was banded on the mill (10-20°C) and other components were added and allowed to disperse by separating and recombining the band of material just before it passed through the nip of the two rolls. When these were uniformly dispersed, the peroxide was added and dispersed in a similar manner.

Flat rectangular sheets of about 2mm thickness were fabricated from the milled compositions by curing and moulding at 170°C for 30 minutes under a pressure of approximately 7 MPa.

Rectangular sheet specimens with dimensions 30 mm x 13 mm x 1.7 mm (approx) were cut from the moulded sheets and fired under slow firing conditions (heating from room temperature to 1000°C at a temperature increase rate of 12°C/min followed by holding at 1000°C for 30 minutes) or fast firing conditions (putting sheets into a pre-heated furnace at 1000°C and maintaining at that temperature for 30 minutes). After firing, each sample took the form of a ceramic char. The change in linear dimensions caused by firing was determined by measuring the length of the specimen before and after firing. An expansion of specimen caused by firing is reported as a positive change in linear dimensions and a contraction (shrinkage) as a negative change in linear dimensions.

Table 1: Compositions A, B, C and D

	Composition (weight %)				
	1	1	В	C	, D
EP Polymer	18		18	18	18
EVA Polymer	4.5		4.5	4.5	4.5
Ammonium Polyphosphate	27		27	27	27
Talc	25		40	25	-
Mica	•			-	25
Alumina Trihydrate	15			, -	15
Magnesium Hydroxide	-			15	=
Other Additives (Stabilisers, Coagent, Paraffinic Oil)	8		8	8	8
Peroxide	2.5		2.5	2.5	2.5
TOTAL	100		100	100	100
Firing Condition	Slow	Fast	Slow	Slow	Slow
Change in linear dimensions when ceramified - %	-2.9	2.0	0.2	6.7	-2.1

On firing at 1000°C, the compositions A, B, C and D transform into hard and strong ceramics that retain the initial shape with minimum dimensional changes.

Example 2

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Specimens of nominal dimensions 30 mm x 13 mm x 1.7 mm, made from compositions A, B, C and D by curing and moulding at 170°C for 30 minutes under a pressure of approximately 7 MPa, were placed on a rectangular piece of refractory so that their long axis was perpendicular to one edge of the supporting refractory block and a 13 mm long portion of each specimen was projecting out from the edge of the supporting refractory block. They were then heated at 12°C per minute to 1000°C and maintained at that temperature for 30 minutes in air. Specimens of all four compositions did not fuse and produced a coherent self-supporting porous ceramic that retained the shape of the specimen prior to exposure to elevated temperatures. Visual inspection revealed that the unsupported span of each specimen remained in place without bending over the edge of the refractory support due to its own weight.

Example 3

A copper conductor of 1.5 mm2 cross section was insulated with a layer of 0.5 mm wall thickness of a ceramifiable composition E (Table 2). A second layer of the composition A was extruded directly over the layer of composition E to provide a composite insulation wall thickness of 1.0 mm. This insulated conductor was twisted together with three other insulated conductors made in the same way to form an assembly of four insulated conductors.

The assembly of twisted, insulated conductors was then sheathed with a commercially available halogen-free, low-smoke, low-toxicity thermoplastic compound, forming a finished cable. Three segments of this cable were then subjected to the circuit integrity test of AS/NZS3013:1995.

The test requires the cable segments to be energised at 240 Volts and then subjected to a furnace test of 2 hours duration to reach a final temperature of 1,050°C, and then a water jet spray for 3 minutes.

Three segments of cable made and tested as described were able to maintain circuit integrity and thus meet the requirements of the circuit integrity test of AS/NZS3013:1995. A comparative cable was produced and subjected to the same test using only insulating material of Composition E and was found to perform unsatisfactorily.

Table 2: Composition E

	wt.%
EP Polymer	19
EVA Polymer	5
Clay	10 .
Talc	10
Mica	- 20
Alumina Trihydrate	10
Calcium Carbonate	10
Silicone Polymer	. 5
Other Additives, (Stabilisers, Coagent, Paraffinic Oil)	8.4
Peroxide	2,6
TOTAL	100

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Finally, it is to be understood that various alterations, modifications and/or additions may be made to the compositions, without departing from the ambit of the present invention as disclosed herein.

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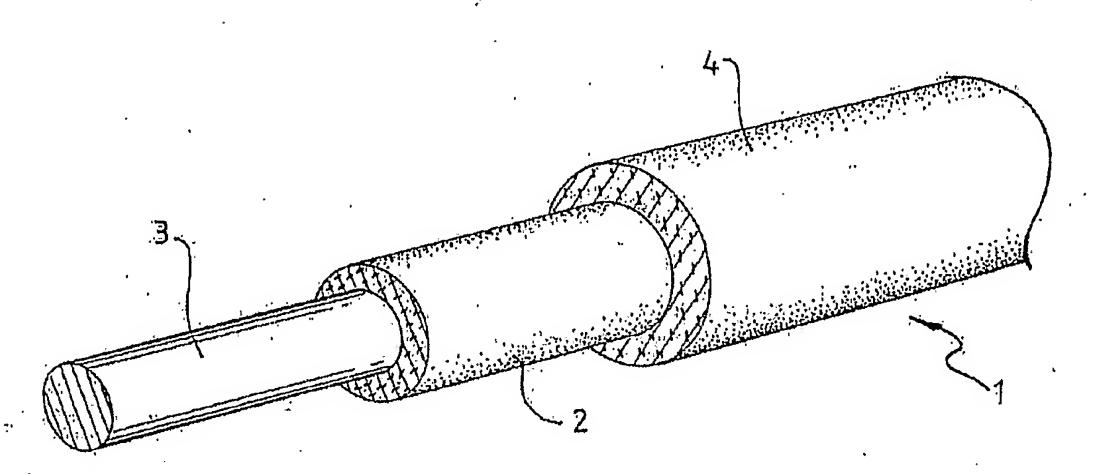


Fig. 1

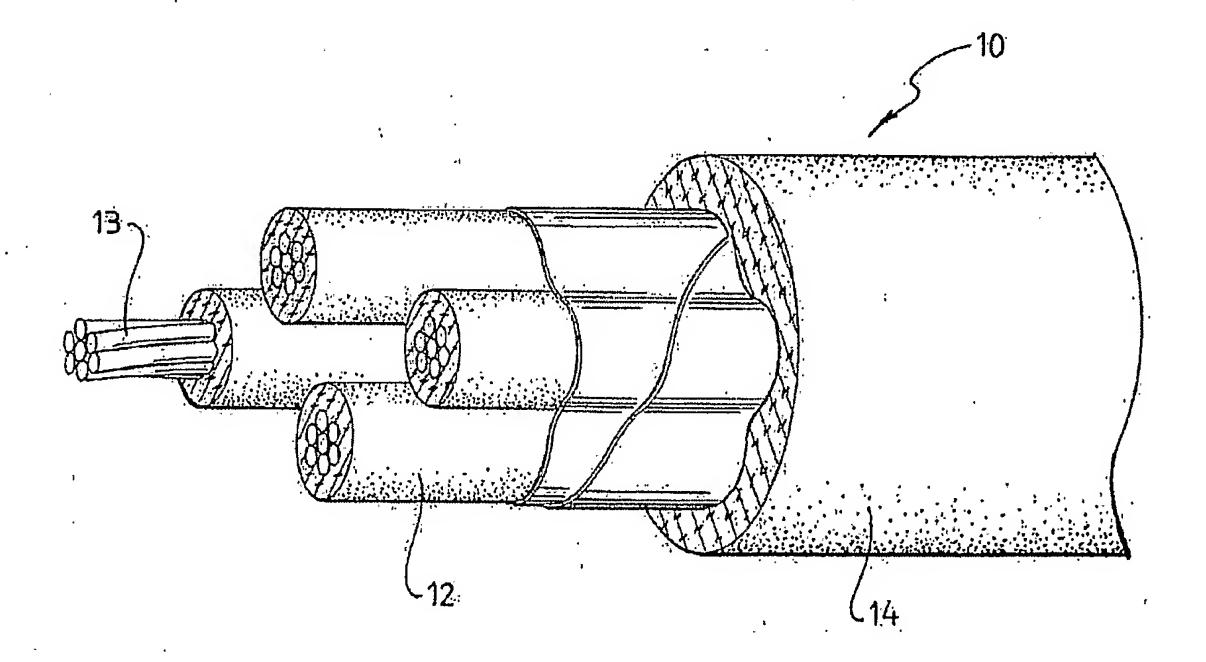


Fig. 2

